

L159,368



# PATENT SPECIFICATION

NO DRAWINGS

L159,368

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## COMPLETE SPECIFICATION

### Substituted Phenols

We, STANDARD OIL COMPANY, a corporation of the State of Indiana, 910 South Michigan Avenue, Chicago, Illinois 60680, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to high molecular weight substituted phenols and more particularly pertains to novel substantially aliphatic hydrocarbon polymer-substituted phenols having substituent groups of fifty or more carbon atoms, a novel method of preparing these alkyl phenols and derivatives of these novel high molecular weight phenols.

Alkyl substituted phenols obtained by alkylation of phenol with olefins of rather low molecular weight such as propylene, butylenes, amylene, diisobutylene, triisobutylene and  $C_8$  to  $C_{12}$  polymers of n-butene in the presence of 0.5 to 1.0 weight per cent  $BF_3$  based on total of reactants at reaction temperatures are disclosed in U.S. Patent No. 2,398,253. This patent discloses optimum alkylation conditions for reaction of the  $C_8$  to  $C_{12}$  olefins with phenol: that the olefin should be added rapidly to the mixture of phenol and  $BF_3$ , the reaction should be concluded shortly after the addition of olefin has been completed, the reaction temperature should not exceed  $70^\circ C$ , and that not more than 0.5 weight per cent  $BF_3$  based on total reactants should be used. There is also disclosed in the said U.S. Patent that the use of high temperature, long reaction time, more than equal molar proportions of phenol or olefin and/or high catalyst concentration leads to formation of low melting products and/or dialkyl phenols.

In U.S. Patent No. 2,671,117 there is disclosed a method of preparing  $C_{10}$  to  $C_{30}$  alkyl substituted phenols by alkylating phenol with a  $C_{10}$  to  $C_{30}$  olefin polymer of propylene,  $C_4$  olefins and mixtures thereof at 60 to  $100^\circ C$ , using a phenol to polymer mole ratio of from 2 to 6 moles phenol per mole of polymer in the presence of  $AlCl_3 \cdot HSO_4$  as catalyst.

We have found that Friedel-Crafts catalysts,  $H_2SO_4$  and sulfonic acid modified ion exchange resins when used in an attempt to prepare  $C_{50}$  and higher alkyl phenols from  $C_{50}$  and higher polypropylenes or polyisobutylenes and the hereinafter defined copolymers of propylene or isobutylene with other copolymerizable monomers results in alkyl phenol yields of 10 to 20 weight per cent based on those  $C_{50}$  and higher polymeric alkylating agents. We have also found the use of less than about 0.1 mole of  $BF_3$  per mole of those  $C_{50}$  and higher polymeric alkylating agents to be substantially ineffective for producing  $C_{50}$  and higher alkyl phenols. We have also found, when using  $BF_3$  as alkylation catalyst that at reaction temperatures in excess of about  $150^\circ F$ . (about  $65^\circ C$ .) the  $C_{50}$  and higher polymeric alkylating agent, especially polyisobutylenes and isobutylene copolymers whose polymer units predominate in isobutylene units, fragment drastically and there is produced a mixture of low molecular weight phenols. For example, when alkylating phenol with a polyisobutylene of about 855 number average molecular weight (a number average carbon content of about  $C_{60}$ ) in the presence of 0.5 mole  $BF_3$  per mole of polyisobutylene at  $150^\circ F$ , the resulting alkylated

phenol product has a number average molecular weight of only about 315 corresponding not to a  $C_{60}$  alkyl phenol but rather a  $C_{16}$  alkyl phenol.

In a rather recent publication BORON FLUORIDE AND ITS COMPOUNDS AS CATALYSTS IN ORGANIC CHEMISTRY, by A. V. Topchiev, S. V. Zavorodnii and Ya. M. Paushkin (translated by J. T. Greaves), Pergamon Press (1959), Chapter V, at page 155, the authors state that higher olefins alkylate phenols in the presence of  $BF_3$  but indicate that high yields, 80%, are obtainable only when  $BF_3$  is used as 70 to 90% phosphoric acid saturated with  $BF_3$ .

However, we have found that  $C_{30}$  and higher substantially aliphatic hydrocarbon polymer substituted phenols can be prepared by alkylation of phenol with, *inter alia*, polymers and copolymers of propylene and butenes, such as 1-butene and isobutylene as hereinafter defined in the presence of  $BF_3$  as catalyst at temperatures below about 150°F. using one or more mole of phenol per mole of the polymeric alkylating agent taking into account the phenol in the  $BF_3$ -phenol complex. Where more than one mole of phenol is used per mole of polymeric alkylating agent, phenol *per se* plus the phenol in the phenol- $BF_3$  complex comprises the total moles of phenol. All the phenol can be supplied as a mixture of phenol- $BF_3$  complex in phenol or phenol plus the 1:1 phenol- $BF_3$  complex can be separately added to supply the molar excess of phenol. When equal molar proportions of phenol and polymer are used, the 1:1 phenol- $BF_3$  complex can be used to supply all the phenol.

The present invention accordingly provides a process of preparing a substantially aliphatic olefin hydrocarbon polymer-substituted phenol having in the polymer substituent a number average carbon content of at least 50 carbon atoms which comprises reacting phenol with a substantially aliphatic olefin polymer hydrocarbon alkylating agent having 50 to 20,000 carbon atoms in the presence of  $BF_3$  in the range of 0.1 to 1.1 mole thereof and from 1 to 4 moles of phenol per mole of said polymer alkylating agent at a temperature in the range of from 30 to 180°F and thereafter removing  $BF_3$  and unreacted phenol from the reaction product.

For the purposes of this invention the  $C_{30}$  and higher substantially aliphatic hydrocarbon polymeric alkylating agents and the resulting substituents on the substituted phenol have a number average carbon content in the range of 50 to 20,000, that is, correspond to a number average molecular weight of about 700 to about 300,000. It will be recognized that those polymeric alkylating agents vary from moderately viscous liquids such as a Saybolt Second Universal (SSU) viscosity of 7000 to 8000 at 100°F. (300 to 350 SSU viscosity at 210°F.) for a  $C_{30}$  polymer to very viscous liquid and even semi-solid for a  $C_{250}$  polymer and to solids for higher carbon content molecules such as are present in butyl rubber. The alkylated phenol products produced by this invention are not obtained in 100 per cent yields based on the polymeric olefin alkylating agent, but do approach 90 to 95% of theory based on the unsaturated molecule content of the polymeric alkylating agent.

The products are also referred to hereinafter as polyalkenyl substituted phenols, in order to denote that they are phenols substituted by a polymeric chain derived from an alkene; for example, those products wherein the substituent polymeric chain is a polypropylene are also referred to as polypropenyl substituted phenols and those products wherein the substituent polymeric chain is a polybutene are also referred to as polybutenyl substituted phenols.

It will also be appreciated that polymeric products generally are not composed of a single molecular weight molecule but rather are mixtures of polymeric molecules having different molecular weights. Hence, the polymeric alkylating agents and the substituents on the alkylated phenols are described with respect to size as "number

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The upper limit of such polar groups in the polymeric molecule or substituent groups is normally not more than 10 weight per cent based on the weight of the hydrocarbon portion of the polymeric molecule or substituent groups.

At last 75%, by molar proportion, of the hydrocarbon units in the substantially aliphatic olefin hydrocarbon polymer should be derived from a mono-olefin.

The substantially aliphatic olefin hydrocarbon polymer alkylating agents, therefore also the substituent groups, can be derived from petroleum fractions of  $C_5$  to  $C_{200}$  and higher carbon content which have at least 75 per cent of its component molecules as mono-olefinic compounds, from polymers of  $C_2$  to  $C_{30}$  mono-olefins and especially useful are polymers of the terminally unsaturated mono-olefin hydrocarbons illustrated by ethylene, propylene, 1-butene, isobutylene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers having 50 to 20,000 or more carbons obtained from mono-olefins having internal unsaturation such as 2-butene, 3-pentene and 4-octene, as contrasted to terminal unsaturation, are useful sources for the polymeric alkylating agents.

The substituent groups and the polymeric alkylating agents can also be derived from unsaturated monomers copolymerizable with the foregoing mono-olefins. Such copolymerizable monomers can be aromatic olefins, cyclic olefins and olefins containing two or more double bonds. Illustrative of such copolymers are, for example, those obtained by the copolymerization of isobutylene with styrene, isobutylene with butadiene, propylene with isoprene, ethylene with piperylene, isobutylene with chloroprene, isobutylene with  $\alpha$ -methyl styrene, isobutylene with  $\alpha$ , $\beta$ -dimethyl styrene, 1-hexene with 1,3-hexadiene, 1-octene with 1-hexene, 1-heptene with 1-pentene, 3-methyl-1-butene with 1-octene, 3,3-dimethyl-1-pentene with 1-hexene, isobutylene with styrene and piperylene, ethylene with vinyl chloride, and ethylene with vinyl acetate, among others.

Ideally, for the alkylation of a phenol all the polymeric molecules in a polymer should be mono-olefinic. However, it is sufficient for the purposes of this invention that at least 75% and preferably at least 80% or up to 85%, of the molecules of the polymeric alkylating agent contain one double bond, i.e. are mono-olefinic. Proportions of polar groups containing monomers copolymerizable with olefinic hydrocarbons can be readily selected so that the polar group content does not exceed the aforementioned basis of 10 weight per cent. Likewise the mole ratios of mono-olefin monomer and dienes, trienes, etc. polyenes can be selected to obtain polymers suitable as alkylating agents. The methods of preparation of the foregoing substantially aliphatic hydrocarbon polymers are well known to those skilled in the polymer art. The polymeric substituents of the alkylated phenol influence the thermal stability and oil solubility of the alkylated phenols and their derivatives intended for use as lubricant oil addition agents and hence the selection of type and proportion of monomers copolymerizable with mono-olefins are selected with this in mind. However, where the alkylated phenols and their derivatives are intended for use other than as lubricant addition agents such as for anti-oxidants for elastomeric polymers (especially natural and synthetic rubbers and vinyl polymers), plasticizers, and ingredients of functional fluids, the oil solubilizing and/or thermal stabilizing influence of the polymeric substituent is not a factor of importance.

The manner in which the ingredients for the alkylating process of this invention are combined is not critical but certain orders of adding or combining ingredients provide advantage especially for high utilization of reactants and for commercial operation. The less viscous polymeric alkylating agents, i.e. those within a SSU viscosity range of 8000 to 12000 at 100°F. for example, can be used direct without dilution. When such less viscous polymeric alkylating agents are used, phenol and the polymeric alkylating agent can be combined in the necessary molar ratios, generally molten phenol is added to the polymer, and then the amount of  $BF_3$  catalyst is added. This manner of combining reactants and  $BF_3$  catalyst does not make efficient use of  $BF_3$  because of the phenol dilution effect of the polymeric alkylating agent. It is desirable to separately add the required amount of  $BF_3$  as gas to a liquid form of phenol, that is either molten phenol at 108 to 120°F. or a solution of phenol in a small amount of  $C_5$  to  $C_8$  alkane or in light mineral oil such as those from white oil to solvent-extracted SAE 10 grade diluent oil. Then the phenol and phenol- $BF_3$  complex in said liquid form is added to the polymeric alkylating agent or the polymeric alkylating agent is added to the fluid form of phenol. The rate of adding the fluid form of phenol and phenol- $BF_3$  complex to the polymeric alkylating agent or the polymeric alkylating agent to the fluid form of phenol and phenol- $BF_3$  complex does not appear to effect materially the efficiency of the phenol alkylation.



The polymeric alkylating agents more viscous than SSU viscosity range of 8000 to 12000 at 100°F. are advantageously diluted with an inert liquid, desirably a hydrocarbon diluent having a normal (760 mm Hg) boiling point above about 70 to 120°F. and preferably a normal boiling point of the normal C<sub>5</sub> to C<sub>8</sub> alkanes where the diluent is to be removed. Where the resulting alkylated phenol and/or its derivative are to be used as a lubricant additive, diluents comprising substantially saturated aliphatic hydrocarbon polymers having a number average carbon atom content at 50 to 200, specifically mineral oils of the grade from light white oils to solvent-extracted SAE 40, are suitable and solvent-extracted SAE 5 to solvent-extracted SAE 10 grade oils are preferred. These diluents can be used in any suitable amount which will provide a readily processable liquid medium convenient for stirring at 70 to below about 150°F. without excessive consumption of power, readily pumpable under ordinary pumping conditions and readily filterable. The hydrocarbon polymer diluents will normally be present in the range of 15 to 50% by weight of the composition, but with a mineral oil of the grade range of from white oil to solvent extracted SAE 10, preferably 25 to 50%.

The BF<sub>3</sub> catalyst can be readily removed from the product of the alkylation reaction even though complexed with unreacted phenol. For example, the BF<sub>3</sub> can be destroyed with water by breaking the phenol-BF<sub>3</sub> complex or taking up free BF<sub>3</sub> to form a BF<sub>3</sub> complex different than the phenol-BF<sub>3</sub> complex. Desirably, the different complex is a solid complex not soluble in the reaction medium and preferably is an NH<sub>3</sub>-BF<sub>3</sub> complex. Because of the ability of the C<sub>5</sub> and higher substantially aliphatic hydrocarbon polymer substituted phenol product to form water-in-oil emulsions, removal of either BF<sub>3</sub> or unreacted phenol from the alkylated phenol product through the use of water is not preferred for this reason. Thus, it is preferred to neutralize BF<sub>3</sub> and/or break the phenol-BF<sub>3</sub> complex by the use of materials which react with BF<sub>3</sub> and form an insoluble solid BF<sub>3</sub>-containing product readily separable from the alkylation product by means applicable to the separation of solids from liquids such as by centrifugation, filtration, decantation, classification, etc. For this preferred neutralization of BF<sub>3</sub>, ammonia and lower alkyl primary amines are preferred.

Since some of the molecules of the polymeric alkylating agent are non-reactive because of their saturation and/or steric hinderance of the chain double bond, it is desirable in some cases to recover the resulting alkylated phenol substantially free from reaction diluent and from the non-reactive portion of the polymeric alkylating agent. In such a case the C<sub>5</sub> to C<sub>8</sub> normal alkane boiling range diluent is used to dilute the polymeric alkylating agent and to dissolve phenol and/or phenol-BF<sub>3</sub> complex used to furnish BF<sub>3</sub> catalyst. After the completion of the reaction, BF<sub>3</sub> is neutralized by the preferred technique whereby a solid insoluble derivative of BF<sub>3</sub> results, preferably by injecting ammonia gas into the reaction mixture, and the resulting mixture can then be subjected to separation of the undissolved solid derivative of BF<sub>3</sub> from the liquid portion of the neutralization reaction. The unreacted phenol is removed suitably by distillation desirably aided by means which, in effect, enhance vaporization, such as reduced pressure (vacuum distillation) and the use of inert gas or steam injection at atmospheric or reduced pressure. Steam stripping or steam distillation for phenol removal is preferably conducted above 210°F. before separation of the insoluble solid derivative of BF<sub>3</sub> obtained from neutralization because not only is phenol readily and efficiently removed, but also the insoluble BF<sub>3</sub> derivative of neutralization agglomerates and makes the remaining liquid more readily filterable. Agglomeration of the particles of the solid derivative form of BF<sub>3</sub>, especially the NH<sub>3</sub>-BF<sub>3</sub> and lower alkyl (C<sub>1</sub> to C<sub>4</sub>) primary amine complexes with BF<sub>3</sub> can also be accomplished during inert gas stripping of phenol at 350 to 500°F.

Thus, in a preferred process according to the present invention the hydrocarbon alkylating agent is polypropylene or polyisobutylene of a number average molecular weight in the range of 700 to 2800, the amount of phenol is, in the case of polyisobutylene, 2.0 to 4.0 moles per mole of polyisobutylene, the BF<sub>3</sub> is neutralized with ammonia, the unreacted phenol is removed by distillation at 350 to 500°F aided by inert gas injection during which the solid ammonia-BF<sub>3</sub> particles agglomerate, and the phenol-free reaction product is filtered to remove said solid ammonia-BF<sub>3</sub> product. Agglomeration of said insoluble BF<sub>3</sub> complexes can also be accomplished at lower temperature, e.g. 210 to 350°F, by the use of steam. Where filtration is the solid-liquid separation means used, the NH<sub>3</sub>-BF<sub>3</sub> particles forming during the BF<sub>3</sub> neutralization are extremely small and render filtration very difficult, if not impossible, to carry out in the absence of providing conditions causing agglomeration of the fine insoluble, solid BF<sub>3</sub> neutralization products.

The steam distillation or stripping is desirably conducted so that a minimum of

- water accumulates in the steam treated reaction mixture. Preferably the steam stripping or distillation is conducted at 300°F. and above, in the range of 300 to 350°F., so that later drying of the steam stripped product is facilitated and the aforementioned  $\text{BF}_3$  neutralization product agglomeration is attained. Drying is accomplished by injecting an inert gas such as nitrogen or mixtures of nitrogen and carbon dioxide, into the steam treated product before or after solid-liquid separation, preferably before, and preferably at 300 to 500° F. although a temperature above 200°F., say 250°F. and higher is suitable where drying only is to be accomplished. The higher drying temperatures result in shorter drying time and, conversely, the lower drying temperatures result in longer drying time.
- The unreactive low molecular weight portion of the polymeric alkylating agent can be removed by distillation preferably aided by steam or inert gas stripping. When alkylated phenols are prepared in light oil diluents, such products can be contacted with silica gel and the silica gel eluted with hexane, heptane, octane, etc. The contacted and eluted silica gel is further treated with ether to obtain an ether solution of the alkyl phenols. Evaporation of the ether leaves the alkylated phenol product. The alkylated phenols prepared in the presence of  $\text{C}_3$  to  $\text{C}_8$  alkanes as reaction diluents can be recovered free from unreactive polymer by the same technique after removal of the reaction solvent.
- By definition, the polymeric alkylating agent is a substantially aliphatic hydrocarbon polymer. Desirably the polymeric alkylating agent is derived from propylene or butenes such as isobutylene or mixtures of 1-butene, 2-butene and isobutylene such as are present in a butane-butene fraction, as the principal or sole monomer. Preferably the polymeric alkylating agent is derived from mainly propylene or said butenes as one monomer and a rather minor portion of a second copolymerizable comonomer so that there is present in the polymer molecules from 90 to 100% units of propylene or said butenes and from 0 to 10% units of the second monomer. The polymeric alkylating agents predominantly of units of said butenes are the most susceptible to fragmentation during the alkylation reaction. When these predominantly butene polymeric alkylating agents are used as alkylating agents, care should be exercised in the selection of such alkylation conditions as reaction temperature and  $\text{BF}_3$  content of alkylation reaction mixture. Although the amount of  $\text{BF}_3$  used as catalyst and based on the polymeric alkylating agent can be varied from 0.1 to 1.1 mole per mole of polymeric alkylating agent, the lower of these mole ratios, e.g. 0.2 to 0.6, result in less fragmentation of said more susceptible fragmenting polymeric alkylating agents. In general, reaction temperatures in excess of about 150°F. need not be used and the alkylations even with said polymeric alkylating agents more susceptible to fragmentation desirably are carried out at 140°F. and below, and preferably at 30 to 120°F. To reduce the fragmentation during alkylation of phenol with the more susceptible polymeric alkylating agents whose molecules consist predominantly of said butene units, phenol desirably is used in an amount greater than a 1 to 1 ratio, preferably in a ratio of 1.5 to 3 moles phenol per mole of polymeric alkylating agent. Alkylation of phenol according to the process of this invention at the preferred reaction temperature range minimizes substantially the fragmentation of the polymeric alkylating agents predominating in either propylene units or units of said butenes. It will be understood that the process of this invention has as its main objective the preparation of alkyl phenols having an alkyl substituent of 50 carbon atoms and above up to 20,000. Hence, to achieve this objective a polymeric alkylating agent with substantially more than 50 carbon atoms can be used under conditions providing fragmentation thereof as long as a substantial yield, about 50% yield of the  $\text{C}_{50}$  alkyl phenol ( $\text{C}_{50}$  number average carbon content) or higher carbon content alkyl phenol is produced. A secondary objective is of course to conduct the alkylation with the polymeric alkylating agents more susceptible to fragmentation under conditions suppressing fragmentation. As will hereinafter be demonstrated by the use of various combinations of reaction temperature, mole ratios of phenol and  $\text{BF}_3$  catalyst to the polymeric alkylating agent conditions for alkylation according to the purposes of this invention can be chosen to tolerate various degrees of fragmentation of the polymeric alkylating agent, and still attain the aforementioned primary and secondary objectives.
- The present invention also provides, as a new composition of matter, a substantially aliphatic olefin hydrocarbon polymer (as hereinbefore defined)-substituted phenol having a polymer substituent which is derived from a mono-olefin and which has a number average carbon content in the range of 50 to 20,000 carbon atoms.
- Fragmentation does not appear to occur with any selection with respect to any particular molecular weight within molecules of any particular number average mole-

5 cular weight polymeric alkylating agent. That is, fragmentation does not appear to  
occur more severely with the higher or lower molecular weight members of a polymeric  
mixture predominantly of butene units. This can be readily demonstrated by a com-  
parison of the molecular weight distribution of a particular number average molecular  
weight polymeric alkylating agent having predominantly butene units against the  
molecular weight distribution of the substituent group of the resulting alkylated phenol  
derived from that polymeric alkylating agent where both distributions are plotted with  
molecular weight units as the abscissa and per cent units as the ordinate. When such  
a comparison is made, the shapes of the distribution curves will be found to be sub-  
stantially the same, but with the curve of distribution of the polymeric substituent  
10 group of the alkylated phenol product being shifted slightly to the left. The shift to  
the left of the molecular weight distribution of the polymeric substituent on the phenol  
with respect to the molecular weight distribution of the starting polymeric alkylating  
agent amounts to a lower number average molecular weight of 0.1 to 1.0% for poly-  
meric alkylating agents having predominantly propylene units and 8 to 20% lower  
15 number average molecular weight for polymeric alkylating agents having predominantly  
butene units, i.e. said butene-1, butene-2, isobutylene and mixtures thereof at controlled  
conditions to achieve the aforementioned secondary objective. Said slightly lower  
number average molecular weight of polypropylene or predominantly propylene poly-  
meric alkylated phenol appears to correlate to the splitting off of a  $C_4H_9$  group, most  
likely as tertiary-butyl groups near the double bond in the polymer molecule since  
evidence of such a tertiary-butyl moiety has been found.

The best mode found for conducting the alkylation process of this invention com-  
prises separately adding  $BF_3$  gas to a fluid form of phenol in an amount of phenol to  
provide the phenol to polymeric alkylating agent desired and the mole ratio of  $BF_3$   
25 to polymeric alkylating agent desired. The phenol plus phenol- $BF_3$  complex or phenol-  
 $BF_3$  1:1 complex is added to the diluted or undiluted polymeric alkylating agent at  
60 to 150°F. and the temperature of the resultant mixture is adjusted with or without  
heat removal to maintain the desired reaction temperature up to but not exceeding  
about 120°F. Unlike prior art processes, it is advantageous to hold the resulting mixture  
30 at reaction temperature, and especially 100 to 140°F. for several (2 to 5 hours) to  
increase yield of the desired alkylated phenol. Ammonia or lower ( $C_1$  to  $C_4$ ) alkyl  
primary amine is injected into the reaction mixture 2 to 5 hours after the phenol and  
 $BF_3$  has been added for the purpose of neutralizing the  $BF_3$ . Thereafter, inert gas or  
steam stripping of the reaction mixture is conducted at about ambient pressure for  
35 0.5 to 5 hours at a temperature of 210°F. and above as aforementioned, until no  
further phenol appears in the condensate. Usually low molecular weight portions of the  
unreacted polymeric alkylating agent and low molecular weight fragments thereof are  
also removed by the steam stripping ahead of phenol and some slightly higher mole-  
40 cular weight materials may come over with the phenol but these portions of the  
polymeric alkylating agent remain liquid whereas phenol solidifies upon cooling. After  
the phenol has been removed, the remaining portion of the reaction mixture is dried,  
0.5 to 2 hours at 300 to 500°F., aided with injection of inert gas such as nitrogen,  
ordinarily will be adequate. The dried mixture is then filtered. When the  $C_3$  to  $C_8$   
45 boiling range alkane is used as reaction diluent, the alkane diluent is removed by  
evaporation, distillation or inert gas stripping prior to the steam, or inert gas phenol  
stripping and after neutralizing the catalyst. Filtration of the dried product removes  
the insoluble  $BF_3$  neutralization product. The alkylated phenol product is a relatively  
viscous liquid and the light oil solution of alkylated phenol, where light oil is used as  
50 reaction solvent and retained, is also relatively viscous at even 210°F. Thus filtration  
with the product or light oil solution at 250 to 350°F. can be used to advantage in  
facilitating the filtration.

As aforementioned, the  $BF_3$  catalyst is preferably charged with a liquid form of  
phenol for then the  $BF_3$  is not a gas but rather is complexed with phenol. The phenol-  
55  $BF_3$  complex contains equimolecular portions of  $BF_3$  and phenol. Where it is desired  
to use one mole each of phenol and  $BF_3$  per mole of polymeric alkylating agent, e.g.  
in the alkylation of phenol with polypropylenes and copolymers predominating in  
propylene units, one mole of  $BF_3$  for each mole of liquid form of phenol are combined  
by adding  $BF_3$  gas to the liquid form of phenol. For the use of one or more moles of  
60 phenol and less than one mole of  $BF_3$  catalyst per mole of polymeric alkylating agent,  
the 1:1 phenol- $BF_3$  product can be diluted with additional phenol until the mixture  
has the desired ratio of phenol and  $BF_3$  and aliquot portions of this mixture are used  
to provide both the phenol and  $BF_3$  catalyst. Also, the precise molar portions of  
phenol and  $BF_3$  to be used in the alkylation reaction are combined by adding a  
65 weighed amount of  $BF_3$  gas to a liquid form of phenol. Alternately, where one gram



5 mole of a polybutene or copolymer predominating in units of butenes is used with 2.5 gram moles of phenol as the selected molar excess of phenol for alkylation and 0.3 gram mole of  $\text{BF}_3$  is selected as the level of catalyst, 20.3 grams (0.3 gram mole)  $\text{BF}_3$  gas can be added to a liquid form of phenol containing at least 0.3 gram mole phenol, and the resulting product and additional phenol to provide the 2.5 moles thereof are charged separately. However, it is more convenient to combine the total amount of  $\text{BF}_3$  with the total amount of phenol to be used and then charge together to the alkylation reactor. We have found that a weighed amount of  $\text{BF}_3$  gas can be injected into molten phenol at 108 to 120°F. or a solution of phenol at 100 to 120°F. without loss of  $\text{BF}_3$  as long as at least equimolecular portions of phenol and  $\text{BF}_3$  are used. The preparation and storage of the compositions containing the  $\text{BF}_3$  and phenol under moisture free conditions is preferred to prevent decomposition of  $\text{BF}_3$  by hydrolysis.

10 The following alkylations of phenol with a polypropylene (number average molecular weight of 800) in the presence of  $\text{BF}_3$ -dimethyl ether complex mixed alkane sulfonic acids and sulfonic acid modified ion exchange resin as catalysts are given to show the substantial ineffectiveness of these materials to promote the formation of  $\text{C}_{30}$  and higher alkyl phenols.

#### $\text{BF}_3$ Etherate Catalyst

20 To a tared flask fitted with a dropping funnel, stirrer, thermometer and heating mantel there is charged 188 grams (2.0 gram moles) phenol. The phenol is heated until all of it melts, about 110°F. Then, without further heating 140 milliliters (154.3 grams)  $\text{BF}_3$  dimethyl etherate is added in 85 minutes by means of a dropping funnel. Thereafter, a solution of 1600 grams (2 gram moles) of 800 number average molecular weight polypropylene in 1000 milliliters of n-hexane is added over 130 minutes by means of a dropping funnel to the mixture of phenol and  $\text{BF}_3$ -etherate while the mixture is stirred. The mixture becomes deep purple in color as the polymer solution is added. After all the polymer solution is added, the reaction mixture is stirred for 75 minutes and then 500 grams of water are added to destroy the  $\text{BF}_3$  catalyst. The resulting mixture is washed several times with water. The water washed mixture is heated to about 300°F. and steam stripped for 3 hours to remove unreacted phenol, the heated to 420°F. and dried with injection of nitrogen. The resulting product is a bright liquid. By analysis, it is found that the bright liquid contains an 8% yield of polypropyl substituted phenol of 838 number average molecular weight,  $\text{C}_{33}$  number average carbon alkyl phenol.

#### Mixed Alkane Sulfonic Acid Catalyst

35 To a tared flask fitted with a dropping funnel, stirrer, thermometer, reflux condenser and heating mantel, there are charged 1800 grams (2.09 moles) polybutene of 860 number average molecular weight (about  $\text{C}_{90}$ ), 300 grams (318 moles) phenol and 120 grams mixed alkane sulfonic acids. The mixture is heated to 260°F. and held at this temperature for 5 hours while vapors from the reaction mixture are condensed and condensate returned to the reaction by the reflux condenser. Thereafter, the reaction mixture is washed twice with water, once with an aqueous solution of 5% sodium bicarbonate and then twice with water. The washed organic liquid is dried at 420°F. aided by nitrogen gas injection. By analysis it is found that the dried organic liquid contained 889 number average molecular weight  $\text{C}_{57}$  alkyl phenol in a yield of 17%.

#### Sulfonic Acid Modified Ion Exchange Resin

50 The are added to a tared flask of the type previously described, 80 grams (0.1 mole) of 800 number average molecular weight polypropylene, 9.4 grams (0.1 mole) phenol and 20 grams of sulfonic acid modified ion exchange resin. This mixture is heated to 230°F., held at 220 to 250°F. for 16 hours and then held at 280°F. for 4 hours. The reaction mixture is filtered and the filtrate is heated to 150 and up to 180°F. in distillation apparatus at reduced pressure, about 10 mm Hg. for 3 hours; however, no phenol condensate is obtained. By analysis it is found that the resulting liquid product contains an 825 number average molecular weight  $\text{C}_{52}$  alkyl phenol in an amount representing a 4% yield.

60 The results of the foregoing preparations are not indicative of feasible catalytic routes to  $\text{C}_{30}$  and higher alkyl phenols. In contrast to the foregoing, comparison of the results of the following illustrative examples of the process of this invention clearly indicate a feasible and advantageous route to the  $\text{C}_{30}$  and higher alkyl substituted phenols.

## EXAMPLE 1

To a glass flask fitted with a stirrer, thermometer, heating mantel and dropping funnel there are added 1600 grams (2.0 moles) polypropylene and 800 number average molecular weight (number average carbon content about 57) and 1000 milliliters n-hexane. The resulting polymer solution is stirred slowly at ambient temperature while 210 milliliters (258.3 grams) of a mixture of phenol and phenol-BF<sub>3</sub> complex providing a total of 1.975 moles phenol and 1.07 moles BF<sub>3</sub> is slowly added over 165 minutes by means of the dropping funnel. The heat of reaction raised the temperature ultimately to about 110°F. About 3.5 hours of vigorous stirring is required after all of the phenol and phenol-BF<sub>3</sub> has been substituted.

The catalyst is destroyed by the addition of water. Then the organic liquid product is washed several times with water. A hazy liquid resulted from this washing indicating some suspended water. The hazy liquid is heated to distill off the hexane and then dried at 300 to 350°F. By analysis the alkyl phenol in the dried organic liquid is found to have a number average molecular weight of 854 (894 is theoretical). The oxygen content of the dried product is found by analysis to be 1.67% by weight indicating the presence of 89% by weight alkyl phenol, 100% 854 number average molecular weight alkyl phenol has an oxygen content of 1.875 weight per cent. The remaining 11 weight per cent consists essentially of unreactive polypropylene. The 854 number average alkyl phenol product has a number average carbon content in the alkyl substituent of 54 or a number average propylene units of 18. By infrared spectrum analysis of the dried product it is determined that the C<sub>54</sub> alkyl substitution is more than 95% para.

By contacting the above product having 89% of the 854 number average molecular weight alkyl phenol and 11% unreactive polypropylene with silica gel, followed by washing with n-hexane to remove the unreactive polypropylene by dissolving in n-hexane, extracting the silica gel-alkyl phenol residue with diethyl ether and evaporating the ether extract, the residue is substantially liquid alkyl phenols having a number average molecular weight of 854.

Hereinafter number average molecular weight will be designated "NAMW" and number average carbon content will be designated "NACC".

## EXAMPLE 2

To apparatus described in Example 1 there are added 141 grams (1.5 moles) phenol, 600 milliliters of n-hexane, and a solution of 1600 grams 800 NAMW polypropylene in 600 milliliters n-hexane. The mixture is stirred and heated until the phenol is dissolved, about 120°F. Thereafter without adding heat BF<sub>3</sub> gas is injected into the solution until about 1.5 mole is added. The resulting solution is pink. The resulting solid is vigorously stirred for 90 minutes and then 600 grams of water are added to destroy the catalyst. The water-organic liquid mixture is transferred to a separatory funnel, the first added water removed and the organic liquid is washed several times with water. After removing the last water wash, the organic liquid is permitted to stand for 16 hours to allow suspended water particles to settle out so that this water also can be removed.

The water washed organic liquid is heated to distill off hexane and then steam stripped for 105 minutes. Thereafter, the organic liquid residue is heated to 250°F. under reduced pressure in vacuum distillation apparatus for about 60 minutes to insure removal of water, phenol and light fractions of the unreactive polypropylene. The resulting liquid product is an orange-brown liquid and is found by analysis to contain 855 NAMW alkyl phenol.

## EXAMPLE 3

The process of Example 1 is repeated except that the 800 NAMW polypropylene is combined with 800 grams of solvent-extracted SAE5W grade hydrocarbon oil; the phenol plus phenol-BF<sub>3</sub> complex is added in 130 minutes. This reaction mixture is noticeably more viscous than that of Example 1 and the temperature of the mixture did not increase as much as in Example 1. Water again is used to destroy the catalyst, and to wash the oil solution of product. However, a water-in-oil emulsion formed which did not break on standing for about 16 hours.

In contrast to the foregoing, the solution of nonyl phenol in solvent-extracted SAE5W grade oil can be mixed with water in a volume amount equivalent to that used above. A water-in-oil emulsion does not form but rather water droplets are suspended and readily separate from the oil.

The water-in-oil emulsion is treated by ammonia gas injection during vigorous stirring. The organic liquid phase became a golden yellow in color. Thereafter, the



mixture is heated to about 350°F. and nitrogen gas is injected into the liquid until about 30 minutes after increase in water condensate ceases. Thereafter, the liquid is filtered through a bed of "Celite" (Registered Trade Mark) and a bright (clear) organic liquid is obtained having 854 NAMW alkyl phenol dissolved in solvent-extracted SAE5W oil.

## EXAMPLE 4

To a flask, as described in Example 1, there is added 400 grams (0.5 mole) of 800 NAMW polypropylene. The polypropylene is heated to 150°F. and 52 milliliters of a liquid phenol having 2 moles phenol for each mole  $\text{BF}_3$  is added slowly over 30 minutes by way of a dropping funnel. The liquid phenol- $\text{BF}_3$  mixture provides 0.5 mole phenol and 0.25 mole  $\text{BF}_3$ . After addition of phenol and  $\text{BF}_3$ , the resulting mixture is vigorously stirred for 5 hours, and its temperature is maintained between 140° and 150°F. Thereafter, ammonia is injected into the liquid reaction mixture until 300°F. about 0.3 mole  $\text{NH}_3$  is added, then the reaction mixture is steam stripped at 300°F. for about 3 hours, filtered and the filtrate stripped by nitrogen gas injection into the liquid at 300°F. for about 3 hours. The dried liquid product contains 892 (theory is 894) NAMW alkyl phenol and has an oxygen content of 1.65 weight per cent (theory for 892 NAMW is 1.792) indicating that the liquid product has 92% of the 892 NAMW alkyl phenol.

## EXAMPLE 5

The process of Example 4 is repeated except that 447 grams solvent-extracted SAE5W grade oil are added to the polypropylene. The resulting dried oil solution contains about 47% 892 NAMW alkyl phenol and has a viscosity of 1343 SSU at 100°F. and 82 SSU at 210°F.

## EXAMPLE 6

To a flask of the type hereinbefore used, there are added 800 grams of 800 NAMW polypropylene and 536 grams solvent-extracted SAE5W grade oil. While stirring the oil-polypropylene mixture, 105 milliliters (128 grams) of the phenol plus  $\text{BF}_3$  described in Example 4 are added in two 52.5 milliliter portions in five minutes. Slow stirring is continued for 30 minutes. Then vigorous stirring is carried out for about 4 hours. During the vigorous stirring, the reaction mixture temperature increased from ambient temperature, about 78°F., to about 113°F. Thereafter, ammonia is injected into the reaction mixture and the temperature thereof increased to 130—135°F. The ammonia injection is continued until the color of the reaction mixture turns from red to golden yellow. The ammonia neutralized reaction mixture is heated to 300°F. and steam stripped for 4 hours, stripped with nitrogen for 90 minutes and filtered. The resulting product, 892 NAMW alkyl phenol dissolved in solvent-extracted SAE5W grade oil has a viscosity of 3898 SSU at 100°F. and 130 SSU at 210°F.

## EXAMPLE 7

To apparatus of the type previously described, there are charged 70 grams (0.75 mole) phenol and 500 milliliters n-hexane. This mixture is stirred and heated until the phenol dissolves and thereafter without further heat input  $\text{BF}_3$  gas is injected into the solution until about 0.75 mole is charged. By means of a dropping funnel a solution of 1100 grams (1.0 mole) of 1100 NAMW polypropylene in 600 milliliters hexane is charged in 90 minutes. The reaction mixture became dark in red in color. The reaction mixture is stirred for about 16 hours without addition of heat and remains at ambient temperature 72 to 75°F. for the 16 hours. The catalyst is then destroyed by adding 500 milliliters of water to the reaction product and the resulting mixture is stirred for 30 minutes, transferred to a separatory funnel, the water layer removed and the organic layer (hexane solution) is washed several times with water. The water washed hexane solution is dried over magnesium sulfate. The dried hexane solution is transferred to distillation apparatus and hexane is removed by distillation. The residue is heated at reduced pressure but little phenol is recovered. The hexane and phenol free residue is found to have a 1108 SSU viscosity at 210°F., and by analysis to contain 0.75% oxygen and alkyl phenol of 1140 NAMW. From the oxygen by analysis and calculated oxygen content of 1140 NAMW alkyl phenol, it is determined that the hexane and phenol free residue contains 52% 1140 NAMW alkyl phenol. A 1140 NAMW alkyl phenol has an alkyl size of 74 NACC.

The 1140 NAMW alkyl phenol in the hexane and phenol free residue of Example 7 can be recovered by contacting it with silica gel, washing the silica gel-alkyl phenol with n-hexane to remove unreacted and unreactive polypropylene, extracting the silica gel-alkyl phenol residue with ether and evaporating the ether.

## EXAMPLE 8

To apparatus of the type previously described, there are charged 100 milliliters n-hexane and 200 grams of a light oil solvent-extracted (SAE5 grade) solution of 70,000 NAMW polybutene (mostly polyiso butylene) containing about 20 weight per cent of said polybutene. This mixture is stirred until a homogeneous appearing solution is formed at ambient temperature, 72 to 74°F. Thereafter, a liquid mixture obtained by dissolving 20 grams phenol in 10 milliliters of a phenol-BF<sub>3</sub> product containing the ratio of two moles phenol and one mole BF<sub>3</sub> is added to the solution of said polybutene. The mixture is stirred for 5 hours and then neutralized with ammonia. The neutralized mixture is heated from ambient temperature to 300°F., stripped with steam for 45 minutes and then stripped with nitrogen at 320°F. for 60 minutes. The nitrogen stripped product is filtered at 300—320°F. through a bed of "Celite." The filtered product is clear, has an oxygen content of 0.55 per cent by weight, a viscosity of 609 SSU at 210°F. and a viscosity of 38,880 SSU at 100°F.

## EXAMPLE 9

There is charged to apparatus previously described 100 milliliters n-hexane and 200 grams of the light oil solution of 70,000 NAMW polybutene described in Example 8. The resulting solution is stirred and cooled to 36°F. and 10 grams of an 8 mole phenol—1.0 mole BF<sub>3</sub> product diluted with 30 grams phenol is added to the solution of said polybutene. The temperature of the reaction mixture increased slowly from 36°F. to about 90°F. while stirring for about 5 hours. The hexane is then removed by distillation. The hexane-free residue at 300°F. is stripped by steam injection for 135 minutes and then by nitrogen injection for 90 minutes. The nitrogen-stripped residue is filtered at 290—300°F. The filtrate is a bright, clear, amber colored liquid having a viscosity of 3315 SSU at 210°F. The alkyl phenol in this product is of much higher molecular weight than that in the product of Example 8 as the difference in magnitude between the 210°F. viscosities clearly indicate.

## EXAMPLE 10

Two hundred grams of butyl rubber cubes are dissolved in 2 liters of hexane. This hexane solution is charged to apparatus of the type previously described. The solution is stirred and heated to 80°F. Without any further heating, 144 milliliters, 165 grams of a phenol-BF<sub>3</sub> product having one mole BF<sub>3</sub> for each 6 moles phenol (this supplies 1.57 moles phenol) is added rapidly to the hexane solution of butyl rubber at 80°F. The resulting mixture is stirred for 20 hours substantially at ambient temperature (72°F). The resulting mixture is neutralized with ammonia; hexane is driven off at 100°F. As the hexane is driven off, 1000 grams of solvent-extracted SAE5W grade oil is added. The resulting solution in solvent-extracted SAE5W oil is found by analysis to have a hydroxy number of 4.0 (4 milequivalents of KOH per gram of product) and an oxygen content of 0.403 per cent weight. The alkyl phenol in said solution in solvent-extracted SAE5W grade oil has an alkyl group made up primarily of units of isobutylene and minor amounts of C<sub>4</sub> diene in the ratios present in the butyl rubber.

## EXAMPLES 11 TO 13

In each of these three examples a solution of 1500 grams (0.583 mole) of 2576 NAMW polybutene in 1500 milliliters n-hexane is initially charged to apparatus previously described. Different mole ratios of phenol and BF<sub>3</sub> per mole of polybutene are used at slightly different reaction temperatures. Phenol and BF<sub>3</sub> are added as liquid mixtures of phenol and phenol-BF<sub>3</sub> complex and each liquid mixture is added slowly by means of a dropping funnel. Stirring of the reaction mixture was continued for about 3 hours after addition of the liquid containing phenol and BF<sub>3</sub>. In each case ammonia is used to neutralize the catalyst, the hexane solvent is distilled from the neutralized reaction product, this hexane free product is stripped with steam at 320°F. for about 135—145 minutes, the steam stripped product is dried at 320°F. aided by nitrogen injection, and the dried product is filtered. There is tabulated in TABLE I the amount of phenol in moles, the amount of BF<sub>3</sub> in moles and the temperature at which the phenol and BF<sub>3</sub> are added. ("Start") the temperature at the end of said addition ("BF<sub>3</sub> in") and the temperature at the end of the 3 hour additional stirring ("End"). Also shown in TABLE I are the respective alkyl phenol NAMW, the alkyl phenol content of the dried product in weight per cent and the number average carbon content (NACC) of the respective alkyl group substituents.

TABLE I  
Phenol Alkylated with 2576 NAMW Polybutene

Example Number	Phenol Moles	BF <sub>3</sub> Mole	Temperature, °F.			Alkyl NACC
			Start	BF <sub>3</sub> in End	NAMW <sup>(2)</sup>	Content
11	1.27	0.32	32	59	2358	75%
12	1.1	0.36	60	90 <sup>(1)</sup>	933	29%
13	1.57	0.345	76	82	1934 <sup>(3)</sup>	87%

- <sup>(1)</sup> Cooled to 70° F.  
<sup>(2)</sup> Theoretical NAMW 2576 + 94 or 2670.  
<sup>(3)</sup> Equal weight parts of this product and solvent-extracted SAE5W grade oil has a viscosity of 477 SSU at 210° F.

EXAMPLE 14

To reaction apparatus as previously described there are added 1500 grams 2576 NAMW polybutene and 1500 grams solvent-extracted SAE5W oil. This polybutene solution in solvent-extracted SAE5W oil is stirred and there is added by means of a dropping funnel a liquid mixture containing 2.4 moles phenol and 0.345 mole BF<sub>3</sub> in 25 minutes causing the temperature of the stirred mixture to increase from 76°F. to 82°F. Stirring is continued for 150 minutes after said phenol and BF<sub>3</sub> addition. Thereafter the resulting product mixture is neutralized with ammonia, the neutralized product is steam stripped at 320°F. for 2 hours and dried at 320°F. aided by nitrogen injection for one hour. This steam and nitrogen stripping resulted in a 144 gram weight loss. The dried product is filtered. The dried product has a viscosity of 521 SSU at 210°F. and contains about 40.4% alkyl phenol.

5 10

EXAMPLE 15

To a reaction kettle there is charged 125 pounds (0.061 pound mole) of the 2040 NAMW polybutene and 125 pounds of solvent extracted SAE 5W oil. This mixture is stirred and heated to 92°F. Then while the oil solution of polybutene is at 92°F., 25 pounds of liquid mixture providing 0.165 pound moles phenol and 0.0355 pound

15



moles  $\text{BF}_3$  is added. The resulting mixture is stirred for 3 hours during which the temperature of the reaction mixture increases from 92 to 118°F. The reaction product is then stripped with nitrogen at 118°F. for 20 minutes, neutralized with ammonia and stirred under a nitrogen gas blanket for 3 hours. The neutralized reaction product is heated to 254°F. and steam is injected into the liquid. Steam stripping is conducted for 5.25 hours over a temperature range of 256° to 300°F., 300°F. for the last three hours. Then the reaction vessel contents are heated to 250°F. and nitrogen gas is injected into the liquid in the vessel for 4 hours to aid in drying. The dried product is filtered. There is recovered 247 pounds of crystal clear dried product containing 43% alkyl phenol (polybutenyl phenol). The dried product has a specific gravity at 77°F. of 0.8897 and a viscosity of 493 SSU at 210°F.

By infrared spectrum analysis, it is determined that the polybutenylphenol of Example 15 is more than 95% p-polybutenylphenol.

To demonstrate the reproducibility of results of the alkylation process of this invention, there is shown the results of three preparations of polybutenylphenol using a polybutene of 2040 NAMW, phenol and  $\text{BF}_3$  in the mole ratios of 1:2.7:0.337. The quantity of ingredients in each preparation are varied and the first is carried out in hexane as reaction solvent which is removed by distillation and the last two are carried out in SAE 5W oil as reaction solvent to produce a solution of the polybutenylphenol in SAE 5W oil. However, the polybutenylphenol product produced in the last two preparations are isolated free from SAE 5W oil, unreacted and unreactive polybutene and it is this product whose characteristic is reported. Each of the three preparations is conducted by adding a liquid phenol- $\text{BF}_3$  composition to the polybutene in hexane or SAE 5W oil, the reaction mixtures are stirred for about 2 hours after adding phenol and  $\text{BF}_3$ , neutralization is carried out with ammonia gas, hexane when used is distilled from the neutralized product, steam stripping is not used, but rather agglomeration of the  $\text{BF}_3\text{-NH}_3$  particles is accomplished at 350° to 450°F. while stripping and drying aided by nitrogen injection, and the dried products are filtered. The pertinent data for each of the three preparations are given in TABLE II.

TABLE II

Phenol Alkylated with 2040 NAMW Polybutene

Example Number	Temperature °F.			Alkyl Phenol		Alkyl NACC
	Start	$\text{BF}_3$ in	End	NAMW	Content	
16	76	84	95	1782	70%	118
17	72	82	100	1755	69%	116
18	104	128	122	1752	66%	116

## EXAMPLE 19

To reaction apparatus of the type previously described there are charged 550 grams (0.27 mole) 2040 NAMW polybutene and 500 milliliters hexane. This mixture is stirred at ambient temperature (about 72°F.) until a solution forms. Thereafter with the solution at ambient temperature and with slow stirring 60 milliliters (73 grams) of liquid reaction product of phenol and  $\text{BF}_3$  having 52 grams (0.553 mole) phenol and 21 grams (0.31 mole)  $\text{BF}_3$  is added dropwise. The mole ratio of reactants and catalyst are 2.04 moles phenol and 1.145 moles  $\text{BF}_3$  per mole polybutene. The reaction mixture is stirred vigorously for three hours after the completion of addition of the phenol- $\text{BF}_3$  liquid, temperature increases to about 90°F. The catalyst is destroyed by adding 500 milliliters of water saturated with sodium chloride at 72°F. This mixture of organic and aqueous liquids is stirred vigorously 15 minutes, transferred to a separatory funnel, the aqueous layer removed and the organic layer washed several times with water saturated at 72°F. with sodium chloride. Hexane is removed from the salt-water washed organic liquid by distillation. The organic liquid residue is steam stripped at 280°F. for about three hours and then stripped with nitrogen injection at 300°F. for about three hours. The resulting product has an oxygen content of 1.36 per cent by weight and contains a polybutenyl-phenol of 831 NAMW (oxygen content of 1.92). Thus there is about 71% of the 831 NAMW polybutenyl-phenol in the dried product.

## EXAMPLE 20

To reaction apparatus of the type previously described there are charged 1740 grams (0.85 mole) 2040 NAMW polybutene and 820 milliliters hexane and these materials are stirred until a solution forms. The solution is stirred slowly while over 30 minutes there is added dropwise 222 milliliters (255 grams) of a liquid mixture containing phenol and  $\text{BF}_3$  in the ratio of 4 moles phenol to 1.0 mole  $\text{BF}_3$ . The temperature of the reaction mixture increases from 72°F. (temperature at start of phenol- $\text{BF}_3$  addition) to 90°F. after 2.5 hours of vigorous stirring following phenol- $\text{BF}_3$  addition. The catalyst is destroyed by ammonia gas neutralization. The neutralized mixture is heated to 300°F. and from 160°F. to 300°F. nitrogen gas is injected to remove 600 milliliters hexane. Nitrogen injection at 300°F. and 1.5 cubic feet per hour (measured at 72°F. and atmospheric pressure) for an additional 15 minutes removed the remaining 220 milliliters hexane. The hexane-free organic liquid is steam stripped at 300°F. for 4 hours and then is dried at 300°F. with nitrogen injection at 1.5 cubic feet per hour for one hour. The dried organic liquid is filtered to remove the agglomerates of  $\text{BF}_3\text{-NH}_3$ . The phenol recovered by steam stripping is 110 grams, therefore, of the 160 grams charged 50 grams (0.532 mole) reacted. The dried reaction product is found to contain about 70 mole per cent calculated from its hydroxyl number of 1345 NAMW polybutenyl phenol.

The mole ratio of reactants and catalyst charged expressed on the basis of one mole 2040 NAMW polybutene charged for Examples 19 and 20 are:

Example 19: 1.0 mole polybutene — 2.04 moles phenol — 1.145 mole  $\text{BF}_3$

Example 20: 1.0 mole polybutene — 2.0 moles phenol — 0.5 mole  $\text{BF}_3$

Thus the higher mole ratio of  $\text{BF}_3$  used in Example 19 resulted in a more severe fragmentation of polybutene resulting in 831 NAMW polybutenyl phenol product than did the use of lower  $\text{BF}_3$  ratio in Example 20 producing 1345 NAMW polybutenyl-phenol. However, even the use of one or slightly more than one mole of  $\text{BF}_3$  per mole of polybutene does result in the production of  $\text{C}_{50}$  or higher alkylated phenol. The 831 NAMW polybutenylphenol produced in Example 19 has about 52 NACC (or 13  $\text{C}_4\text{H}_9$  units) and the 1345 NAMW polybutenylphenol has about 88 NACC (or 22  $\text{C}_4\text{H}_9$  units).

## EXAMPLE 21

To reaction apparatus previously described there are charged and stirred 0.735 mole 2040 NAMW polybutene and 1500 milliliters hexane. To this stirred mixture at 82°F. there is added a liquid mixture of 1.98 moles phenol and 0.383 mole  $\text{BF}_3$  over 25 minutes while slowly stirring the reaction mixture. The temperature of the reaction mixture increased from 82°F. to 90°F. in the 25 minutes of phenol and  $\text{BF}_3$  addition. The resulting reaction mixture is then vigorously stirred for 2.75 hours at 90°F. and then neutralized with ammonia. The neutralized mixture is stripped of hexane in 1.25 hours at 320°F. aided by nitrogen gas injection, steam stripped 300 to 320°F. for 2.25 hours and dried at 320°F. for 0.75 hour with nitrogen injection at 5 cubic feet per hour (measured at 77°F. and atmospheric pressure). The dried organic

liquid is filtered to remove solid  $\text{BF}_3\text{-NH}_3$  agglomerated particles. The dry filtrate is found to contain 85 mole per cent yield 1713 polybutene phenol. Equal weight parts of the dried liquid filtrate and SAE 5W grade oil has a viscosity at 210°F. of the 402 SSU.

- 5 In Examples 22 to 31 which follow there is charged 2.7 moles phenol per mole 2040 NAMW polybutene. Equal volumes of hexane and said polybutene are charged and stirred to form the hexane solution. The mole ratio of  $\text{BF}_3$  to said polybutene is varied from 0.63 to 0.38 mole  $\text{BF}_3$  per mole polybutene and the initial temperature ('Start'), temperature at end of phenol- $\text{BF}_3$  addition (" $\text{BF}_3$  in") and temperature at 10 end of 2.5 hours additional stirring ("End") also vary. Otherwise the ammonia neutralization of  $\text{BF}_3$ , removal of hexane reaction diluent, steam stripping to remove unreacted phenol, drying aided by nitrogen injection, and  $\text{BF}_3\text{-NH}_3$  solid removal are all substantially the same as in Example 21. The pertinent data for Examples 22 to 31 are set forth in TABLE III which follows. 5 .10



TABLE III  
Phenol Alkylated with 2040 NAMW Polybutene

Example Number	Phenol <sup>(1)</sup> Moles	BF <sub>3</sub> <sup>(1)</sup> Mole	Temperature °F.			Alkyl Phenol		Alkyl NACC <sup>(4)</sup>
			Start	BF <sub>3</sub> in	End	NAMW <sup>(2)</sup>	Content <sup>(3)</sup>	
22	2.7	0.63	72	80	95	1167	80	76
23	2.7	0.60	140	140	160	595		37
24	2.7	0.53	70	72	72	1825	90	121
25	2.7	0.50	32	73	76	1836	79	122
26	2.7	0.52	72	84	95	1529 <sup>(5)</sup>	98	102
27	2.7	0.52	80	94	100	1027 <sup>(6)</sup>	88	66
28	2.7	0.52	72	80	85	1493 <sup>(7)</sup>	77	99
29	2.7	0.34	76	84	95	1782 <sup>(8)</sup>	83	120
30	2.7	0.34	110	135	140	15614 <sup>(9)</sup>	66	107
31	2.7	0.54	72	72	72	1926	83	129

<sup>(1)</sup> Per mole 2040 NAMW polybutene.

<sup>(2)</sup> Theoretical NAMW: 2040 + 94 or 2134.

<sup>(3)</sup> Mole per cent from hydroxyl number.

<sup>(4)</sup> Approximate-based on C<sub>4</sub>H<sub>9</sub> units.

<sup>(5)</sup> Product has viscosity at 210° F. of 18602 SSU.

<sup>(6)</sup> Product has viscosity at 210° F. of 12183 SSU.

<sup>(7)</sup> Product has viscosity at 210° F. of 17257 SSU.

<sup>(8)</sup> Product has viscosity at 210° F. of 20412 SSU.

<sup>(9)</sup> Product has viscosity at 210° F. of 18978 SSU.

- 5 The high reaction temperature of Example 23 (140—160°F.) results in rather substantial polybutene degradation as the 629 NAMW polybutenylphenol indicates especially when compared to Example 22 (70—95°F. reaction) where substantially the same ratio of  $\text{BF}_3$  to polybutene is used and 1167 NAMW polybutenylphenol is produced. The 2040 polybutene has a NACC of approximately 144. Thus the  $\text{BF}_3$  mole ratio and reaction temperature combinations of Examples 22 and 23 appear to reduce the polybutene chain length to 52% and to 25.7%, respectively. By reducing the catalyst of Example 23 about in half a vast improvement in polybutene degradation is achieved by substantially the same reaction temperature and 0.34 mole  $\text{BF}_3$  of Example 30. Examples 24, 25 and 31 demonstrate substantial reproducibility. When polybutene and polymeric alkylating agents predominating in butene units are used to alkylate phenol in light mineral oil, the reaction temperature appears to have less influence on polymer degradation or fragmentation than above indicated. This is demonstrated by Examples 32 to 46 which follow.
- 10 In the phenol alkylations with 2040 NAMW polybutene in Examples 32 to 46 there is used solvent-extracted SAE 5W grade oil as the polybutene solvent for the alkylation reaction. The oil solvent is not removed and hence the final product has the polybutenylphenol dissolved in solvent-extracted SAE 5W oil. Portions of certain of these solvent-extracted SAE 5W oil solutions of polybutylphenol are processed to remove not only the solvent-extracted SAE 5W oil but also unreacted and unreactive polybutene and to isolate the polybutenylphenol products. Their molecular weights (NAMW) are determined. The alkylation reactions are conducted as hereinbefore described. Phenol and  $\text{BF}_3$  are added slowly as a liquid product to the solution of polymer in oil. Vigorous stirring of the reaction mixture after  $\text{BF}_3$  addition for 2 to 3 hours is employed.  $\text{BF}_3$  neutralization is with ammonia. Unreacted phenol is removed by steam and/or nitrogen-aided stripping at 300 to 450°F. The reaction mixture is dried as needed, and the solvent-extracted SAE 5W oil solution of polybutenylphenol is filtered to remove solid  $\text{BF}_3\text{-NH}_3$ . The pertinent data for Examples 32 to 46 is shown in Table IV. The only new column headings are: "WR oil to PB" to designate the weight ratio of solvent-extracted SAE 5W oil to polybutene used, "% Active in Oil" used to designate the polybutenylphenol weight concentration in the solvent-extracted SAE 5W oil solution and "210°F. SSU" to designate the viscosity of the solvent-extracted SAE 5W oil solutions of polybutenylphenol at 210°F. in Saybolt Seconds Universal.
- 15
- 20
- 25
- 30

TABLE IV  
Phenol Alkylated with 2040 NAMW Polybutene in Solvent-Extracted SAE 5 W Oil

Example Number	Phenol <sup>(1)</sup> Moles	BF <sub>3</sub> <sup>(1)</sup> Mole	Temperature °F.			WR Oil to PB	% Active in Oil	210° F. SSU
			Start	BF <sub>3</sub> in	End			
32	1.35	0.26	82	90	100	0.47 to 1	37	1573
33	2.0	0.25	74	82	100	0.47 to 1	41	1574
34	2.0	0.36	74	80	90	0.47 to 1	47 <sup>(2)</sup>	1568
35	2.7	0.59	78	90	102	1 to 1	39	423
36	2.7	0.52	86	95	102	0.47 to 1	52	1507
37	2.7	0.52	74	80	95	0.47 to 1	50	1662
38	2.7	0.52	90	95	95	0.47 to 1	46	1115
39	2.7	0.48	82	90	100	0.47 to 1	42	1293
40	2.7	0.45	90	104	116	0.67 to 1	39 <sup>(3)</sup>	805
41	2.7	0.34	72	90	115	0.47 to 1	51	1549
42	2.7	0.34	100	122	150	0.47 to 1	41	1163
43	2.7	0.34	74	82	100	0.47 to 1	46 <sup>(4)</sup>	1943
44	2.7	0.34	74	80	95	0.67 to 1	42	985
45	2.7	0.34	110	110	140	0.67 to 1	37	910
46	2.7	0.27	72	90	114	0.47 to 1	49	1655

<sup>(1)</sup> Per mole 2040 NAMW polybutene.

<sup>(2)</sup> Polybutenylphenol free of oil and non-reacted polybutenes: 1529 NAMW.

<sup>(3)</sup> Polybutenylphenol free of oil and non-reacted polybutenes: 1706 NAMW.

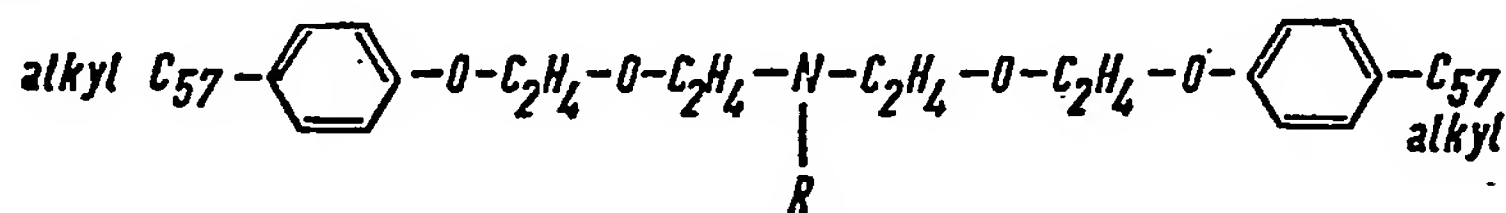
<sup>(4)</sup> Polybutenylphenol free of oil and non-reacted polybutenes: 1755 NAMW.



It will be noted from the 210°F. viscosities of the solvent-extracted SAE 5W oil solutions that the polybutylphenol of Example 32 must have a NAMW above 1706 which is the NAMW polybutenylphenol of Example 40. Using the three NAMW values of Examples 34, 40 and 43 (1529, 1706 and 1755, respectively) it will be seen that high reaction temperatures are not as deleterious when light oil is the reaction diluent as when hexane is the reaction diluent (Examples 23 and 27). It will be noted that when oil is the reaction diluent reaction temperatures in the 122 to 150°F. range do not produce such a drastic molecular weight reduction over reaction temperatures of 74 to 90 as a comparison of the 210°F. SSU values (a qualitative indication of molecular weight of solute) of the solution product of Examples 42 compared with those of Examples 33 and 38 demonstrate.

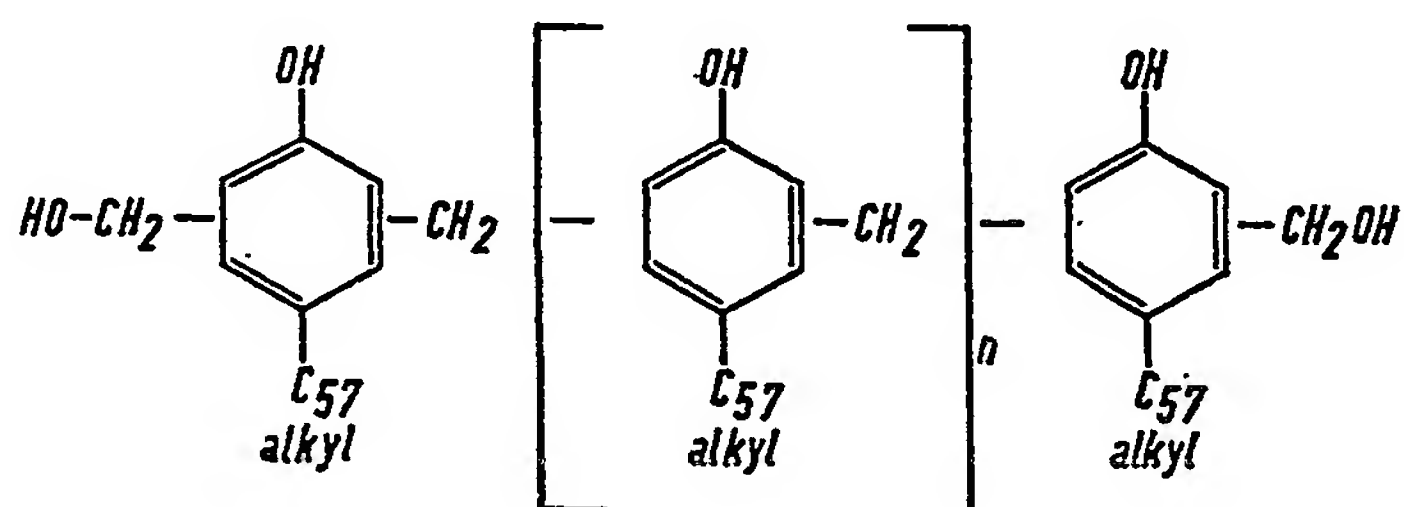
As herein demonstrated novel  $C_{50}$  and higher substantially aliphatic hydrocarbon olefinic polymer substituted phenol, mainly para-substituted, can be produced according to the alkylation process of this invention. Even though under certain demonstrated reaction conditions, i.e. temperature and  $BF_3$  to polybutene or polymer predominating in butene units, there is fragmentation degradation of the polymeric substituent on the phenol with respect to the starting polymeric alkylating agent,  $C_{50}$  and higher substituted phenol can still be produced. In many instances the fragmentation degradation can be tolerated because of the high utilization of the more expensive phenol reactant, or because the alkylphenol product so produced is highly useful or because even the resulting alkylphenol cannot be produced by any other known manner with as readily available alkylating agents. The polybutenes and polypropylenes and a number of copolymers having predominantly units of propylene, the butenes and isobutylene are commercially available products and have been for quite some time. Even the isobutylene-diene elastomeric polymers known as butyl rubbers have been available commercial products for some time. Thus the most preferred conditions of reaction temperature and  $BF_3$  to polymeric alkylating agent are not in general critical for the preparation of  $C_{50}$  and higher carbon content alkylated phenol products. Rather these preferred conditions are used to advantage where it is desired to maximize utilization of phenol and polymeric alkylating agent and produce an alkylated phenol of as high a carbon size alkyl substituent as is feasible.

As hereinbefore disclosed, the  $C_{50}$  and higher alkylphenols are useful intermediates for the preparation of novel products. For example by reacting the  $C_{50}$  and higher carbon alkylphenol as its alkali metal salt with a di(chloroalkyl) ether such as di(2-chloroethyl) ether, di-(3-chloropropyl) ether, di-(2-chloropropyl) ether, and the like there can be produced p- $C_{50}$  and higher alkyl chloroalkoxyalkyl phenates. For example, p-(polypropenyl) phenol whose polypropenyl group has a molecular weight of 798 and a  $C_{57}$  size is reacted with sodium hydroxide in equimolecular proportions to form the sodium  $C_{57}$  alkyl phenate. This sodium phenate is reacted with an equimolar amount of  $\beta$ -dichloroethyl ether at 320 to 340°F. Rapid addition of  $\beta$ -dichloroethyl ether, all at one time, provides a polymeric product through reaction of one chlorine with the sodium phenate and dehydrochlorination of the second chloroethyl group thus forming vinyloxyethyl  $C_{57}$  alkyl phenate monomer which polymerizes. A somewhat slower addition of  $\beta$ -dichloroethyl ether can produce 2,2-di ( $C_{57}$  alkylphenoxy) ethyl ether and especially when less than equimolar amounts of  $\beta$ -dichloroethyl ether are employed. Very slow addition of  $\beta$ -dichloroethyl ether results in the formation of p- $C_{57}$  alkyl  $\beta$ -chloroethoxyethyl phenate. The latter can be reacted with ammonia, primary alkyl amines, diamino alkanes and aza-alkylene-amines such as diethyl triamine and triethylene tetramine to insert nitrogen containing bridges linking two  $C_{57}$  alkyl phenates through a chain having nitrogen-alkoxyalkyl ether groups. For example, ammonia and primary alkyl amines reacted with  $\beta$ -chloroethoxyethyl  $C_{57}$  alkyl phenate can produce:



(I)  
when R is H the reactant is ammonia and where R is alkyl the reactant is primary alkyl amine.

Also the  $C_{50}$  and higher carbon content alkyl phenols of this invention can be reacted with excess formaldehyde in the presence of caustic to produce polyhydroxy compounds having both phenol hydroxy groups and alkanol hydroxy groups as in

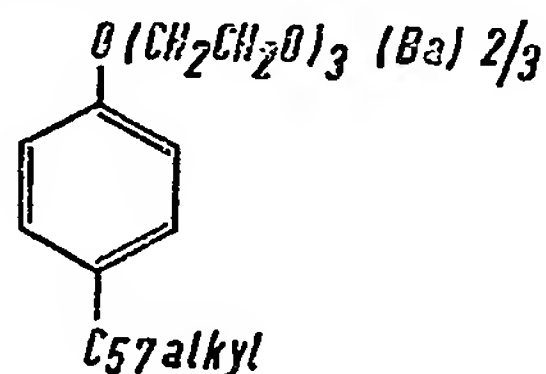


## (II)

where  $n$  is 0 to 5.

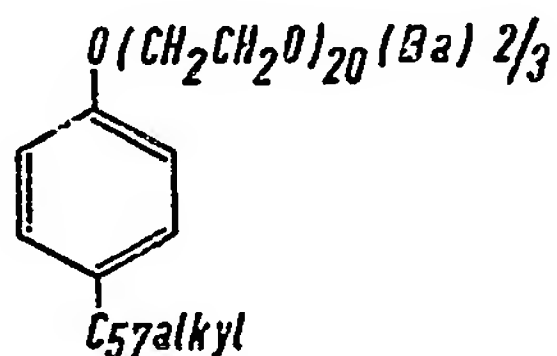
Such compounds can be further reacted by taking advantage of selectivity of reactions common to lower alkanols, either or both of the  $-\text{CH}_2\text{OH}$  groups, and then reacted to form phenate derivatives through reaction of the phenol hydroxy group. For example 2,6-di(2-hydroxy,3-methylol,5- $\text{C}_{57}$  alkylbenzyl) 4- $\text{C}_{57}$  alkylphenol ( $n$  is 3 of Formula II) can be reacted with adipic acid or terephthalic acid in equimolecular portions to form high molecular weight saturated polyesters. Such polyesters can be crosslinked by reacting with a diacid chloride of a dicarboxylic acid.

The  $\text{C}_{50}$  and higher alkylphenols of this invention can be reacted with one or more moles of alkaline earth oxide or hydroxide to form the neutral and over based alkali metal salts. For example, the reaction of one mole  $\text{C}_{57}$  polypropenylphenol with 1.6 moles barium hydroxide produces the corresponding barium phenate having 33% more barium than the exactly neutral barium phenate. Such a high based barium phenate can be used as an antioxidant in crankcase lubricating oil formulations and also provide alkalinity to neutralize acidic combustion products. The high based barium  $\text{C}_{57}$  polypropenyl phenate can also be reacted with an olefin oxide such as ethylene oxide to form barium containing polyglycolate derivatives of the  $\text{C}_{57}$  polypropenylphenol. These barium polyglycolate derivatives of the  $\text{C}_{50}$  and higher alkyl phenols are useful as detergent-dispersants in crankcase lubricant oil formulations. Examples of such a barium polyglycolate derivative are



## (III)

AND



## (IV)

Compound IV prepared by adding ethylene oxide to a 48% solution of high based barium  $\text{C}_{57}$  polypropenylphenol in solvent-extracted SAE 5W grade oil (solution contains 4.7% barium and has a total base number of 36.8) at 330°F. until 20 moles of ethylene oxide per mole of the barium phenate are taken up. The resulting product is grease-like and contains 12.55% oxygen and 3.2% barium. This is a novel grease.

The  $\text{C}_{50}$  and higher alkylphenols of this invention can be converted to an alkali metal phenate and then reacted with carbon dioxide to form the corresponding alkali metal  $\text{C}_{50}$  and higher salicylate which upon acidification yields the  $\text{C}_{50}$  and higher salicylic acid. For example, one mole sodium p- $\text{C}_{57}$  polypropenyl phenate is reacted

with CO<sub>2</sub> at 150 pounds per square inch at 350°F. Upon acidification of the reaction product a 50% yield of m-C<sub>57</sub> polypropenyl o-salicylic acid, identified by infrared spectrum indication of salicylic acid moiety with carboxyl absorption at 1655 Cm<sup>-1</sup>.

5 The C<sub>50</sub> and higher alkylphenols of this invention and the C<sub>50</sub> and higher salicylic acid derivatives thereof can be reacted with formaldehyde and amines having amino groups to form hydroxy C<sub>50</sub> and higher-alkylbenzyl substituted amines and carboxy-  
amide hydroxy C<sub>50</sub> and higher alkylbenzyl substituted amines, respectively. These  
10 substituted amines are not only oil soluble but also function as dispersants-detergents with antioxidant properties for lubricant oil formulations. This subject matter is more fully disclosed and described in our copending Application No. 37002/66 (Serial No. 1,159,369). 10

#### WHAT WE CLAIM IS:—

15 1. A process of preparing a substantially aliphatic olefin hydrocarbon polymer (as hereinbefore defined)-substituted phenol having in the polymer substituent a number average carbon content of at least 50 carbon atoms which comprises reacting phenol  
with a substantially aliphatic olefin polymer hydrocarbon (as hereinbefore defined) alkylating agent having 50 to 20,000 carbon atoms in the presence of BF<sub>3</sub> in the  
20 range of 0.1 to 1.1 mole thereof and from 1 to 4 moles of phenol per mole of said polymer alkylating agent at a temperature in the range of from 30 to 180°F. and thereafter removing BF<sub>3</sub> and unreacted phenol from the reaction product. 20

2. The process of Claim 1 wherein BF<sub>3</sub> is removed by water washing of the reaction product, unreacted phenol is removed by distillation and the BF<sub>3</sub> and phenol-free fraction product is dried.

25 3. The process of Claim 1 wherein BF<sub>3</sub> is neutralized with ammonia, the resulting solid ammonia-BF<sub>3</sub> neutralization product is agglomerated, unreacted phenol is removed by injection of steam, and the resulting mixture is dried at a temperature above 210°F. and the agglomerated solid ammonia-BF<sub>3</sub> neutralization product is removed by filtration. 25

30 4. The process of Claim 3 wherein the removal of water is aided by injecting an inert gas into said heated mixture. 30

5. The process of Claim 1 wherein BF<sub>3</sub> is neutralized with ammonia, unreacted phenol is removed by distillation at 350 to 500°F. aided by inert gas injection during which the solid ammonia-BF<sub>3</sub> particles agglomerate, and filtering the phenol free  
35 reaction product to remove said solid ammonia-BF<sub>3</sub> product. 35

6. The process of Claim 5 wherein the substantially aliphatic olefin polymer alkylating agent is polyisobutylene of a number average molecular weight in the range of 700 to 2800, and the amount of phenol is 2.0 to 4.0 moles per mole of polyisobutylene.

40 7. The process of Claim 1 wherein the substantially aliphatic olefin alkylating agent is polypropylene of a number average molecular weight in the range of 700 to 2800. 40

8. The process of Claim 1 wherein a C<sub>n</sub> to C<sub>n</sub> alkane hydrocarbon is employed as a reaction diluent.

45 9. The process of Claim 5 wherein a mineral hydrocarbon oil of the grade in the range represented by white mineral oil to solvent extracted SAE 10 mineral oil is employed as a reaction diluent. 45

50 10. A substantially aliphatic olefin hydrocarbon polymer (as herein defined)-substituted phenol having a polymer substituent which is derived from a mono-olefin and which has a number average carbon content in the range of 50 to 20,000 carbon atoms. 50

11. The substituted phenol of Claim 10 wherein said polymer substituent is a polyisobutylene of a number average carbon content in the range of 50 to 200 carbon atoms.

55 12. The p-polypropenyl substituted phenols having a number average molecular weight of from 854 to 1140. 55

13. The p-polybutenyl substituted phenols having a number average molecular weight in the range of 933 to 2358.

60 14. A composition comprising a substantially aliphatic olefin hydrocarbon polymer (as hereinbefore defined)-substituted phenol having in the polymer substituent a carbon content in the range of 50 to 200 carbon atoms and a diluent comprising a substantially saturated aliphatic hydrocarbon polymer having a number average carbon content in the range of 50 to 200 carbon atoms said diluents being present in the range of 15 to 50 weight per cent of the composition. 60



15. A solution comprising the composition of Claim 14 dissolved in a mineral oil of the grade range of from white oil to solvent extracted SAE 10 present in an amount in the range of 25 to 50 weight per cent of the solution.

5 16. The composition of Claim 15 wherein the solvent is solvent extracted SAE 5 grade mineral oil. 5

17. A process according to Claim 1 for producing  $C_{50}$  and higher substantially aliphatic hydrocarbon substituted phenols substantially as disclosed and exemplified herein.

10 18. A  $C_{50}$  and higher substantially aliphatic hydrocarbon substituted phenol whenever made by processes according to any of Claims 1 to 9, and 17. 10

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